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Controlled Chemical Polymerization Method for Processing Conducting Polymers

First Year Progress Report

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Contract Number: W7707-032288/A

Contract Scientific Authority: Dr. Colin G. Cameron, (902) 427-1367

Defence R&D Canada – Atlantic

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Abstract

It has been over twenty-five years since Heeger, MacDiarmid and Shirakawa found that polyacetylene could be endowed with near-metallic electrical conductivity following oxidation (or *doping*) with iodine. Since then, there has been a surge in investigation of conducting polymers, most commonly polythiophene, polypyrrole, polyaniline, or their derivatives. Numerous conducting polymer applications have been proposed, ranging from molecular electronics to anti-corrosive agents. The importance and potential impact of the discovery of conducting polymers resulted in Heeger, MacDiarmid and Shirakawa receiving the Nobel Prize in Chemistry (2000). Despite the promise of these new materials, very few viable technologies have emerged from the laboratory proof-of-concept level. It is widely known that one of the most important causes of this failure is the lack of processability of conducting polymers. Bulk polymer can be synthesized in solution by oxidation of the monomer resulting in radical coupling, with the desired product precipitating rapidly as an amorphous powder. Precipitation is driven by π-stacking and Coulombic effects leading to very strong interchain interactions. This in turn precludes conventional thermoplastic or solution processing methods. Several elegant approaches have been developed over the years to reduce π–π interactions in order to generate soluble conducting polymers, however these approaches invariably lead to lower conductivities (due to decreased p-orbital overlap along the backbone) and increased costs. This document describes an alternate, general-purpose route to preparing conducting polymers under processible conditions.

Résumé

Il y a maintenant vingt-cinq ans que Heeger, MacDiarmid et Shirakawa ont découvert qu'on pouvait donner au polyacétylène une conductivité électrique proche de celle des métaux en l'oxydant (ou en le « dopant ») avec de l'iode. Depuis ce temps là, de nombreuses études ont été réalisées sur les polymères conducteurs. Elles portaient généralement sur le polytiophène, le polypyrrole, la polyaniline ou leurs dérivés. On a proposé de nombreuses applications pour les polymères conducteurs, allant de l'électronique moléculaire aux agents anticorrosion. En 2000, Heeger, MacDiarmid et Shirakawa ont reçu le prix Nobel de chimie pour cette découverte importante et son impact potentiel. Malgré la promesse de nouveaux matériaux, très peu de technologies viables ont dépassé le niveau de la validation de principe au laboratoire, et il est bien connu qu'une des raisons les plus importantes est le manque de transformabilité des polymères conducteurs. Les polymères en masse peuvent être synthétisés en solution par oxydation du monomère, condui-

sant à un couplage des radicaux, le produit recherché précipitant rapidement sous forme de poudre amorphe. La précipitation dépend de l'empilement π et d'effets Coulomb, qui conduisent à de très fortes interactions interchaînes qui, à leur tour, empêchent les méthodes classiques de traitement thermoplastique ou en solution. Plusieurs approches élégantes ont été suivies au cours des ans pour réduire les interactions $\pi - \pi$, afin de produire des polymères conducteurs solubles. Ces approches ont toutefois invariablement conduit à une réduction de la conductivité (due à une diminution de recouvrement orbital π le long du squelette) et à des coûts plus importants. Le présent document décrit une nouvelle voie générale pour la préparation de polymères conducteurs et transformables.

Executive summary

Background

There is a class of polymeric materials that share the common feature of a backbone with alternating single and double bonds. The striking feature of these materials is that they can be made to become electrically conductive. Understandably, this has generated a lot of interest since both lightweight electrical conductors and materials with adjustable electronic characteristics would be potentially very useful. However, in the twenty-five years since their discovery, conducting polymers have found few industrial applications, most likely due to their inability to be processed using methods typically used in the plastics industry.

Principal Results

This report concludes the first half of a two-year study in demonstrating methods of making conducting polymers processible. The key to the approach is to cause the polymerization to occur under very gentle, controlled conditions. Such conditions can be achieved by manipulating the balance of oxidized and neutral monomers by the judicious choice of oxidant, and controlling the rate of polymerization with concentration of the reactive oxidized form. This work shows how the controlled growth of polypyrrole can be achieved using phosphomolybdic acid as the oxidant. It goes on to demonstrate that the oxidant can then be removed from the polymer, leaving pristine films. The methodology was also adapted to form interpenetrating networks. Some preliminary work with polythiophene was also done.

Significance of Results

These results are significant since they demonstrate a general method of forming conducting polymers in a processible manner, but without relying on structural modifications to the polymer itself; such modifications often lead to diminished conductivity and other limitations. The successful formation of a conducting polymer interpenetrating network in a thermoset matrix is an important milestone.

Future Work

The second stage of this project will further study the electrical properties of conducting polymer composites. The polymerization of thiophene will also be examined in greater detail.

Michael S. Freund; 2005; Controlled Chemical Polymerization Method for Processing Conducting Polymers; DRDC Atlantic CR 2005-080; Defence R&D Canada – Atlantic.

Sommaire

Contexte

Il existe une classe de matières polymères possédant la caractéristique commune d'un squelette avec alternance de liaisons simples et de liaisons doubles. Ces matières se distinguent par le fait qu'on peut les rendre conductrices de l'électricité. De façon fort compréhensible, ceci a suscité un grand intérêt, puisque des conducteurs électriques légers et des matières avec des caractéristiques électroniques réglables pourraient potentiellement être très utiles. Toutefois, au cours des vingt-cinq années qui ont suivi leur découverte, les polymères conducteurs n'ont reçu que peu d'applications industrielles, probablement à cause de leur incapacité à être transformés au moyen des méthodes généralement utilisées dans l'industrie des matières plastiques.

Résultats Principaux

Le présent rapport est la conclusion de la première moitié d'une étude de deux ans ayant pour objectif de développer des méthodes pour rendre les polymères conducteurs transformables. L'élément clé de cette approche est de provoquer la polymérisation dans des conditions très douces et bien contrôlées. On peut obtenir de telles conditions en modifiant l'équilibre entre les monomères neutres et ceux oxydés, par un choix judicieux de l'oxydant et un contrôle de la vitesse de polymérisation par la concentration de la forme réactive oxydée. Ce travail a montré comment on peut contrôler la croissance du polypyrrole en utilisant de l'acide phosphomolybdique comme oxydant. On y montre aussi que l'oxydant peut être éliminé du polymère, produisant ainsi des couches minces parfaites. Cette méthodologie a aussi été adaptée de manière à former des réseaux interpénétrants. On a aussi fait quelques travaux préliminaires sur le polythiophène.

Importance des Résultats

Ces résultats sont importants, car ils ont mis en évidence une méthode générale de production de polymères conducteurs pouvant être transformés, sans avoir à faire de modifications de la structure même du polymère. De telles modifications conduisent souvent à réduire la conductivité et à d'autres limitations. La formation d'un réseau de polymère conducteur interpénétrant une matrice thermodurcissable constitue une avancée importante.

Travaux Futurs

La deuxième étape du présent projet constituera à étudier les propriétés électriques des composites polymères conducteurs. On étudiera aussi plus à fond la polymérisation du thiophène.

Michael S. Freund; 2005; Controlled Chemical Polymerization Method for Processing Conducting Polymers; DRDC Atlantic CR 2005-080; R&D pour la défense Canada – Atlantique.

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1 Introduction

It has been over twenty-five years since Heeger, MacDiarmid and Shirakawa found that polyacetylene could be endowed with near-metallic electrical conductivity following oxidation (or *doping*) with iodine. Since then, there has been a surge in investigation of conducting polymers, most commonly polythiophene, polypyrrole, polyaniline, or their derivatives. Numerous conducting polymer applications have been proposed, ranging from molecular electronics to anti-corrosive agents. The importance and potential impact of the discovery of conducting polymers resulted in Heeger, MacDiarmid and Shirakawa receiving the Nobel Prize in Chemistry (2000). Despite the promise of these new materials, very few viable technologies have emerged from the laboratory proof-of-concept level. It is widely known that one of the most important causes of this failure is the lack of processability of conducting polymers. Bulk polymer can be synthesized in solution by oxidation of the monomer resulting in radical coupling, with the desired product precipitating rapidly as an amorphous powder. Precipitation is driven by π-stacking and Coulombic effects leading to very strong interchain interactions. This in turn precludes conventional thermoplastic or solution processing methods. Several elegant approaches have been developed over the years to reduce π–π interactions in order to generate soluble conducting polymers, however these approaches invariably lead to lower conductivities (due to decreased p-orbital overlap along the backbone) and are time consuming.

2 Synthetic Background

A proof of concept study has demonstrated an approach that uses an easily processible mixture of monomer (pyrrole) and oxidant (phosphomolybdic acid), which rapidly polymerizes upon solvent evaporation. This approach allows casting, spin-coating, air-brushing and painting of a conducting polymer on arbitrary substrates. The polymer films produced in this way exhibit the same high conductivities, redox and mechanical properties of electrochemically generated thin films, without the need for a conducting substrate, electrolyte and electrochemical equipment.

The nature of this polymerization reaction lends itself to a range of other applications, such as the formation of interpenetrating polymer networks (composites). In this area, polymerization of a polymer within the structure of a different polymer, results in a hybrid material with new and useful properties.

The work described in this document can be broken down into three goals. First, we have investigated the fate of phosphomolybdic acid in the polymer produced. Phosphomolybic acid is a large (diameter of 14 Å), redox active metal-oxygen cluster.

If it remains in the film, it is expected to influence the optical and electronic properties of the material. If absent, the cluster may leave behind a porous film, with unique and interesting properties. Second, we explore the feasibility of forming interpenetrating polymer networks using this reaction. In particular we swell latex (polybutadiene) and allow the polymerization reaction to proceed within the existing latex structure. Third, we focused on demonstrating this approach to another polymer system. Specifically, we use bi-thiophene and ter-thiophene, which have redox potentials near that of pyrrole, which was expected to behave in a similar manner with the same oxidant (phosphomolybdic acid).

3 Goal 1

To determine the fate of phosphomolybdic acid in the chemical preparation of polypyrrole. To determine whether the phosphomolybdic acid was completely removed from the film upon rinsing, or if it stayed trapped within the polymer network.

3.1 Experimental Design

Over the past two decades polyoxometalates have been widely used because of their interesting catalytic properties [1], due to the chemical and electrochemical similarities with metal oxides. Many researchers have attempted to incorporate polyoxometalates into conducting polymers to take advantage of these properties. Recent work in our laboratory has demonstrated that certain polyoxometalates have sufficient oxidizing ability to be used to polymerize conducting polymers. Subsequently, some researchers [2] have reported that the polyoxometales are trapped within the polymer matrix upon electrochemical polymerization of conducting polymers in the presences of the polyoxometalate. However, they also reported that after rinsing the polypyrrole with organic solvents, it is possible to detect the presence of "blue reduced species" of the phosphomolybdic acid, left behind in the solvent. Therefore, there exists some uncertainly over whether the polyoxometalate can be completely removed or not. The aim of the work described in this section is to qualitatively confirm the presence or absence of the polyoxometalate in polypyrrole films upon completion of the rinsing process described below.

3.1.1 Method

Phosphomolybdic acid is the polyoxometalate of choice due to its redox potential relative to pyrrole. Polypyrrole films were prepared by spin coating solutions (1000 RPM) containing pyrrole/THF (180 mM) and phosphomolybdic acid/THF

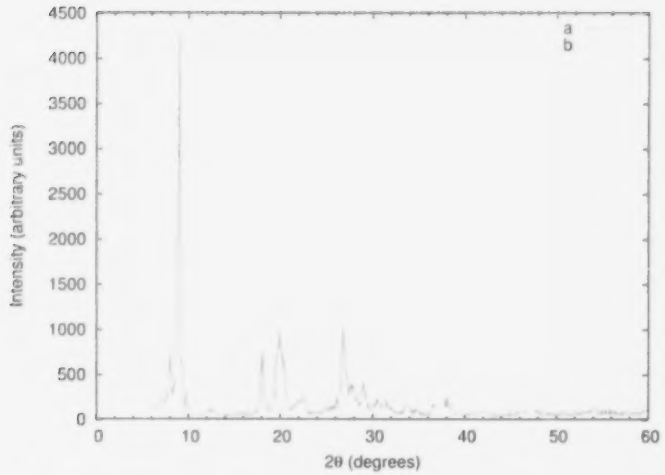

Figure 1: *X-ray pattern of Phosphomolybdic acid: (a) pure state, and (b) previously dissolved in THF.*

(90 mM) onto zero background quartz slides. All slides were rinsed with THF or H_2SO_4 to remove any trace of reduced phosphomolybdic acid. For comparison, polypyrrole was also chemically synthesized using $FeCl_3$ as the oxidant following a method described elsewhere [3, 4], and deposited onto zero background quartz slides.

3.2 Results and Discussion

In order to determine the presence of phosphomolybdic acid in our films, X-ray diffraction was performed. For purposes of comparison, phosphomolybdic acid alone was deposited on quartz slides from THF. Figure 1 shows the X-ray diffraction patterns of both the oxidized and reduced forms of phosphomolybdic acid. The X-Ray pattern for the oxidized form (Figure 1a) shows the characteristic peaks of a highly organized crystalline material as received. The presence of the diffraction peak at $2\theta = 8.95^\circ$ corresponds to the diameter of phosphomolybdic acid ($\approx$ 14 Å), which agrees with the characteristic geometry of the Keggin structure (Figure 2) [5, 6]. The X-ray diffraction pattern of the phosphomolybdic acid cast from THF (Figure 1b) shows broad lines or halos characteristic of an amorphous material rather than the crystalline material observed in Figure 1a. However, the diffraction peak at around $2\theta = 10^\circ$, characteristic of the Keggin structure is still present. A similar pattern has been observed by Otero *et al.* [7] in the crystalline material at elevated temperature and was attributed to the loss of the three dimensional periodicity of the rombohedral structure.

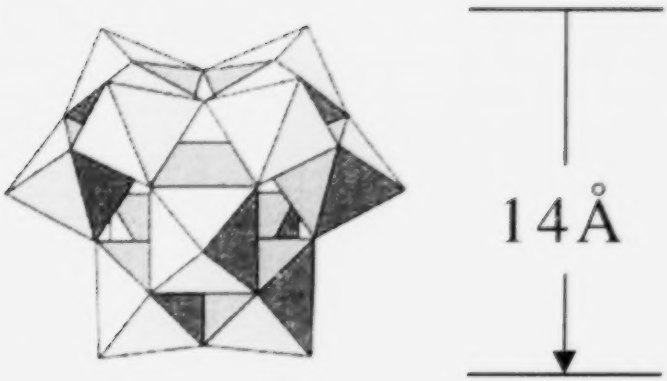

Figure 2: *The α-Keggin structure shown as an assemblage of 12 [MO_6] octahedra and a [XO_4] tetrahedron.*

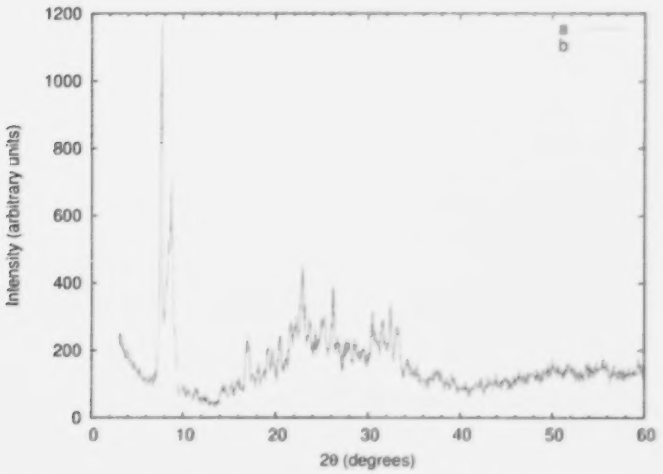

Figure 3: *X-ray pattern of (a) Phosphomolybdic acid in the presence of THF, and (b) Phosphomolybdic acid in its reduced form.*

The X-ray diffraction pattern of the reduced form of phosphomolybdic acid obtained after the polymerization of pyrrole and cast from THF is shown in Figure 3. The broad halo between $2\theta = 15^\circ - 35^\circ$ shows some of the features observed for both the oxidized pure phosphomolybdic acid (Figure 1a) as well as for phosphomolybdic acid cast from THF. All the diffraction lines are much weaker or nearly disappear completely, indicating the loss of the periodicity of the rhombohedral structure. Similar patterns were observed for the reduced form by Otero *et al.* [7].

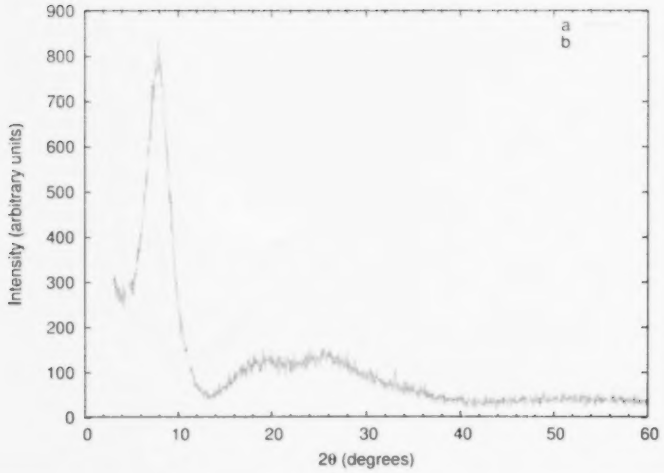

Figure 4: *X-ray diffraction pattern of polypyrrole chemically synthesized with either (a) phosphomolybdic acid or (b) $FeCl_3$.*

The X-Ray diffraction pattern of polypyrrole (Figure 4) prepared chemically using either phosphomolybdic acid or $FeCl_3$ shows an amorphous halo in the region of $2\theta = 15° - 35°$, and these have been attributed to randomly ordered arrays of polymer chains in the literature. The X-ray diffraction pattern of the polypyrrole (prepared using phosphomolybdic acid) shows a clear diffraction peak at $2\theta = 7.95°$ suggesting that either the Keggin structure remains in the film or that an ordered structure is left behind following rinsing. The lack of a corresponding diffraction peak for polypyrrole prepared using $FeCl_3$ as an oxidant supports the assertion that this structure is associated with the polyoxometalate. The sharp diffraction peaks in Figure 4b correspond to the presence of Fe_2O_3, which is likely to be formed by hydrolysis either during the polymerization or during the rinsing of the polymer.

Previous reports by other researchers have suggested that phosphomolybdic acid remains in the film after rinsing with 0.5 M aqueous solution of H_2SO_4. In that particular work, cyclic voltammetry was used to observe the redox activity of phosphomolybdic acid. Our thin films exhibited no such redox activity under identical conditions suggesting that the phosphomolydic acid was removed upon rinsing either with THF or H_2SO_4. In order to explore this further, additional samples were prepared and analyzed by X-ray diffraction before and after rinsing with a 0.5 M aqueous solution of H_2SO_4 (Figure 5). Before rinsing the film, similar features were observed for the phosphomolybdic acid cast from THF. For example the two peaks in the region of $2\theta = 10°$ are present. After rinsing the film, the X-ray pattern (Figure 5b) has the same features as observed for the polypyrrole chemically prepared with phosphomolybdic acid and rinsed with THF. In this case, the absence of fea-

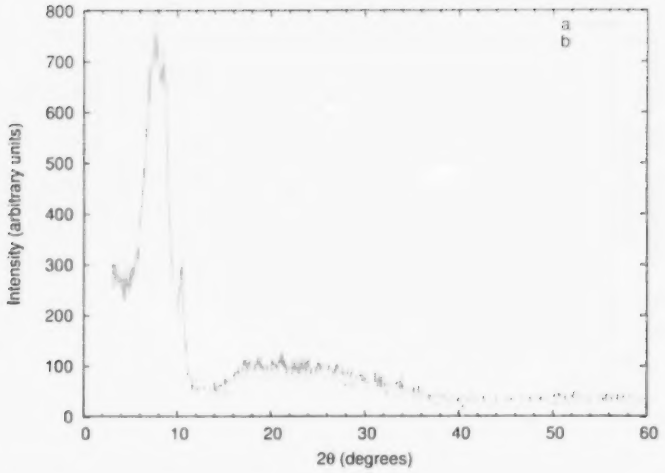

Figure 5: *X-ray diffraction pattern of polypyrrole chemically synthesized with phosphomolybdic acid (a) before and (b) after rinsing with H_2SO_4.*

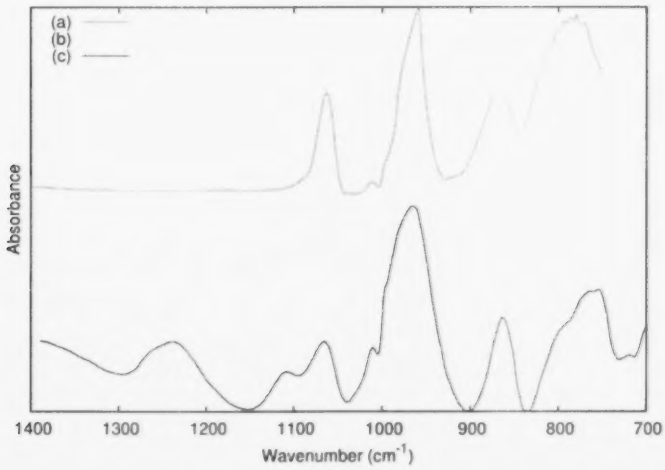

Figure 6: *FTIR spectra of phosphomolybdic acid: (a) as received, (b) after drying, and (c) reduced form.*

tures characteristic of phosphomolybdic acid in either its oxidized or reduced form indicates that under these conditions the Keggin structure of phosphomolybdic acid has been removed. The peak at $2\theta = 7.95°$ may correspond to the templating of the polymer by the Keggin structure of phosphomolybdic acid which is subsequently removed.

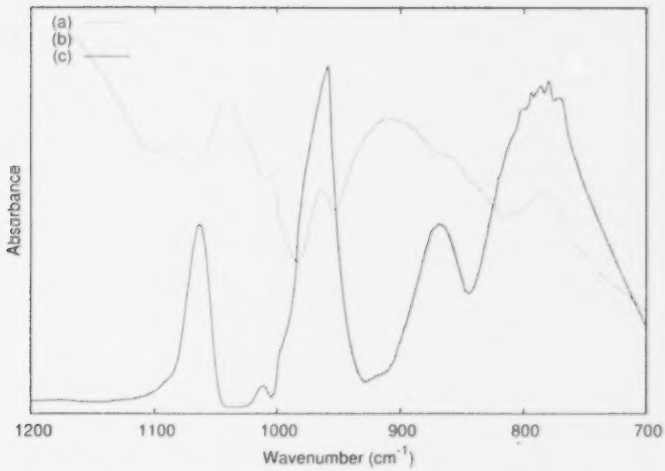

Figure 7: *FTIR spectra of (a) polypyrrole prepared with $FeCl_3$, (b) polypyrrole film formed with phosphomolybdic acid and rinsed with H_2SO_4, and (c) phosphomolybdic acid.*

FTIR was also used to study this system further. The spectra of the oxidized form of phosphomolybdic acid is shown in Figure 6 . The vibration bands observed at 1064 cm^{-1}, 960 cm^{-1}, and 870 cm^{-1} respectively, corresponds to those reported in the literature as the characteristic bands of the Keggin structure [5, 8]. The corresponding FTIR spectrum of the reduced form of phosphomolybdic acid is also shown in Figure 6. As expected, the characteristic vibration bands are also present but the peaks appeared to be much weaker than those of the oxidized form.

The FTIR spectra of polypyrrole (prepared with $FeCl_3$) and polypyrrole film (prepared with phosphomolybdic acid and rinsed with H_2SO_4) are shown in Figure 7. In both cases the vibration bands characteristic of polypyrrole are similar to the ones reported in the literature [4, 9, 10]. The absence of a peak at 1064 cm^{-1} in Figure 7b further supports the conclusion that phosphomolybdic acid is removed upon rinsing.

3.3 Summary

It has been demonstrated that phosphomolybdic acid is removed from polypyrrole films upon completion of a rinsing process (either THF or H_2SO_4.). The presence of diffraction peak after rinsing suggests that the polymer is templated with the Keggin structure which is subsequently removed in the rinsing process. In response to reports claiming that phosphomolybdic acid is trapped within the polymer chains [2], this may have been observed due to incomplete rinsing. They do not re-

port the thicknesses of their films nor do they give the time. Additionally, very thick polypyrrole films, (over 100 nm) may in fact trap in phosphomolybdic acid, which is not completely rinsed out of the film.

4 Goal 2

To explore methods to form a conducting hybrid material (interpenetrating polymer network) that takes on the mechanical properties of the insulating host polymer. To characterize the resulting hybrid material.

4.1 Experimental Design

4.1.1 Synthesis

The present methodology utilizes tetrahydrofuran (THF) to swell poly-isobutadiene (latex) based polymers used as the host material. Swelling of latex in THF allows for rapid loading of phosphomolybdic acid into the latex structure. The loaded latex can then be exposed to pyrrole monomer. Subsequently, polymerization will then take place within the structure of the latex host.

4.1.2 Loading protocol for phosphomolybdic acid

Before the interpenetrating materials could be prepared, it was necessary to determine the maximum amount of phosphomolybdic acid that could be loaded into the latex samples. Several attempts to calculate this value were pursued. Latex samples were left to swell in various concentrations of phosphomolybdic acid in THF. After being rinsed, dried and weighed, the maximum amount of phosphomolybdic acid the latex could absorb was found to be 15% of its original weight. Approximately 30 minutes was necessary the phosphomolybdic acid to load into the latex. Leaving the samples in solution for longer durations of time did not affect the outcome.

4.1.3 Method

Four procedures were explored in an effort to determine the best approach for the formation of an interpenetrating polymer network with the highest conductivity, and most stable mechanical properties. First, simply swelling the latex with a mixture of monomer and oxidant; second, swelling the latex with oxidant and then exposing the loaded latex to a solution of monomer; third, swelling the latex with oxidant followed by drying and exposure to monomer in the gas phase; fourth, exposing the swollen loaded latex to monomer in the gas phase.

In the first approach, a mixture of monomer and oxidant was used following the procedure described by our group previously. Specifically, 90 mM of oxidant and 180 mM of monomer were each dissolved separately in 2 mL of THF (HPLC grade). The two solutions were mixed and latex samples were added to the solution. This approach was unsuccessful since polymerization at the solution/latex interface interfered with swelling of the material.

The second approach involved placing the latex samples in a solution containing the phosphomolybdic acid solution described above. The samples were allowed to swell for 30 minutes. The films turned from yellow to yellow-green and the size of the latex films increased by almost a factor of three. The films were then briefly rinsed and placed in the solution of monomer described above. The polymerization took place mostly in solution and on the surface of latex film, limiting the monomer polymerization inside the latex. After rinsing with THF and drying, the polymer formed on the surface of the latex did not adhere well.

The third approach involved swelling the latex in a solution of phosphomolybdic acid as described in the second approach. The films were then briefly rinsed with THF, dried at room temperature for about 2 hours (films reached their original size after 30 minuntes) and weighed. Subsequently, the dried latex loaded with phosphomolybdic acid were placed in a solution of pyrrole (described above) overnight at room temperature and allowed to swell with the monomer solution. The latex pieces turned from green to black after approximately 30 minutes. The resulting samples were then rinsed with THF for 30 minutes (THF was replaced until there was no blue solution, *i.e.*, reduced phosphomolybdic acid, coming out of the film), dried at room temperature, and weighed. At this point these samples were ready to be characterized.

The fourth approach also involved swelling the latex in a solution of phosphomolybdic acid as described in the second approach. This was followed by placing the swollen films into a container containing vials of THF (to maintain the film in a swollen state and a vial containing pyrrole to provide a constant vapour pressure of the monomer. After allowing the polymerization to occur overnight, the samples were rinsed, dried, rinsed in ethanol (to extract phosphomolybdic acid without swelling), and dried again.

4.2 Results and Discussion

In order to characterize the composite materials formed using these approaches, FTIR spectra, energy dispersive x-ray spectra, and SEM images were used. To investigate the structure of the interpenetrating polymer networks, SEM images were taken of the following samples: latex samples loaded with phosphomolybdic acid,

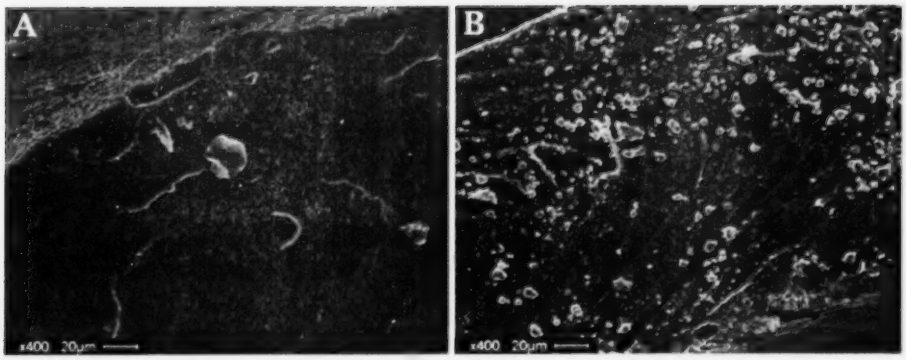

Figure 8: *Edge-view SEM pictures of Au-coated (a) pure latex, and (b) latex with phosphomolybdic acid.*

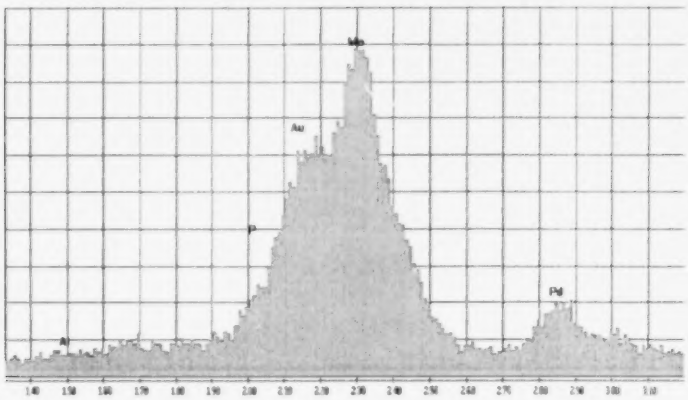

Figure 9: *EDS spectrum of a latex film loaded with phosphomolybdic acid.*

samples yielding interpenetrating polymer networks from the less successful procedures, as well from the more successful procedures. In addition, the elastic properties of the samples were investigated by a stretching the samples and observing the microscopic effects.

Latex films before and after loading with phosphomolybdic acid were analyzed by SEM and BES. Figure 8a shows a cross-section of a latex film, which is relatively smooth and homogeneous. Following loading and drying cross-sections (see Figure 8b) show the presence of phosphomolybdic acid deposits. The EDS spectrum of the deposits (Figure 9) observed in the films shows the presence of molybdenum as well as phosphorous. The ratio between both elements appears to be consistent with the presence of phosphomolybdic acid as expected.

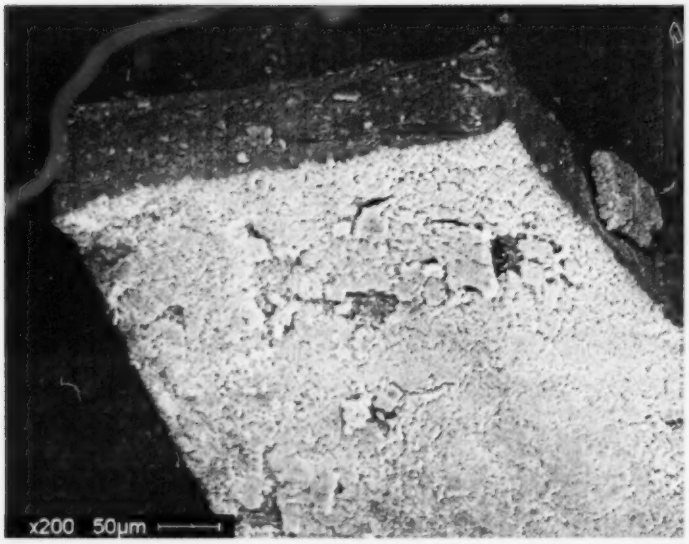

Figure 10: *SEM of phosphomolybdic acid + latex film after soaking in pyrrole monomer and rinsing according to approach #3.*

The samples prepared using the third approach resulted in the formation of black polypyrrole throughout the latex film, however there was no detectible conductivity through the latex. In addition, the polymer adhered poorly to the surface as observed in Figure 10.

Figure 11 illustrates the sample formed following the fourth approach, which successfully produced an interpenetrating polymer network. SEM analysis of the exposed edge (see Figure 12) of the latex film (obtained by freeze fracture) confirms the conducting behaviour of the hybrid material. Conductivity was confirmed by the fact that samples did not require carbon or gold coating prior to SEM and BES analysis indicating that the sample was sufficiently conducting to dissipate the charge even in the center of the cross section. Close inspection of the surface of the latex film clear shows the presence of a polypyrrole film with a thickness of approximately 1 μm. Interestingly, the adhesion of the film is sufficiently strong to survive the large volume change from its swollen to its dried state. For example, the film follows the contours of the surface and appears to cause the underlying latex to pucker. This behaviour is in stark contrast to the surface film observed in Figure 10. These images suggest that the formation of an interpenetrating polymer network in this case dramatically enhances adhesion. Another feature of note in Figure 12 is the even distribution of the conducting polymer in the latex. For example, there are no regions within the latex that appear to charge (*i.e.*, become extremely bright) due to lack of conductivity. This suggests that conducting polymer extends throughout

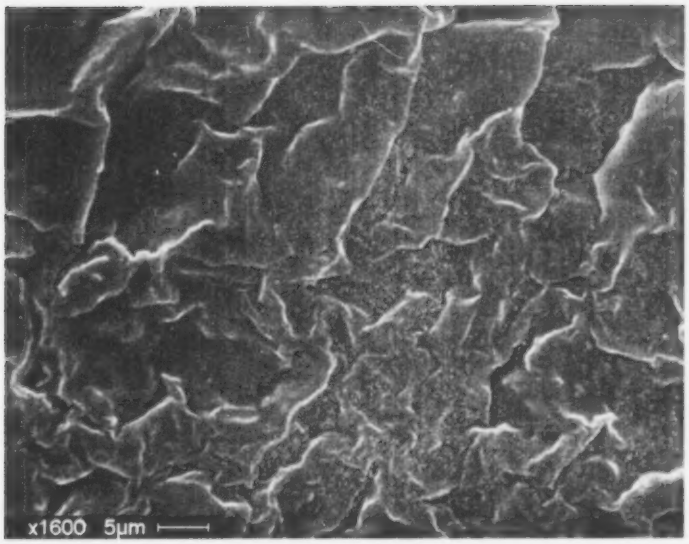

Figure 11: *SEM surface view picture of polypyrrole-latex film following the fourth approach.*

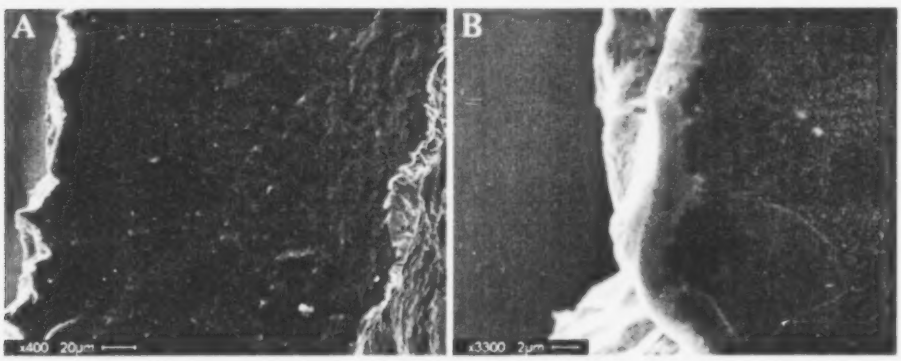

Figure 12: *SEM edge-view picture of polypyrrole-latex film, no carbon coating.*

the structure.

The FTIR absorption spectra (Figure 14) of the following samples were taken: plain latex, latex loaded with phosphomolybdic acid, and the interpenetrating polymer network formed using the fourth approach. The spectra of the interpenetrating polymer network exhibited characteristic vibrations of pyrrole present at 1543 cm^{-1}, 1308 cm^{-1}, 1169 cm^{-1}, and 1041 cm^{-1}, respectively. These values correspond with those reported in the literature [11]. The interpenetrating polymer network spectra also indicated a characteristic band of polybutadiene at 1457 cm^{-1}. This

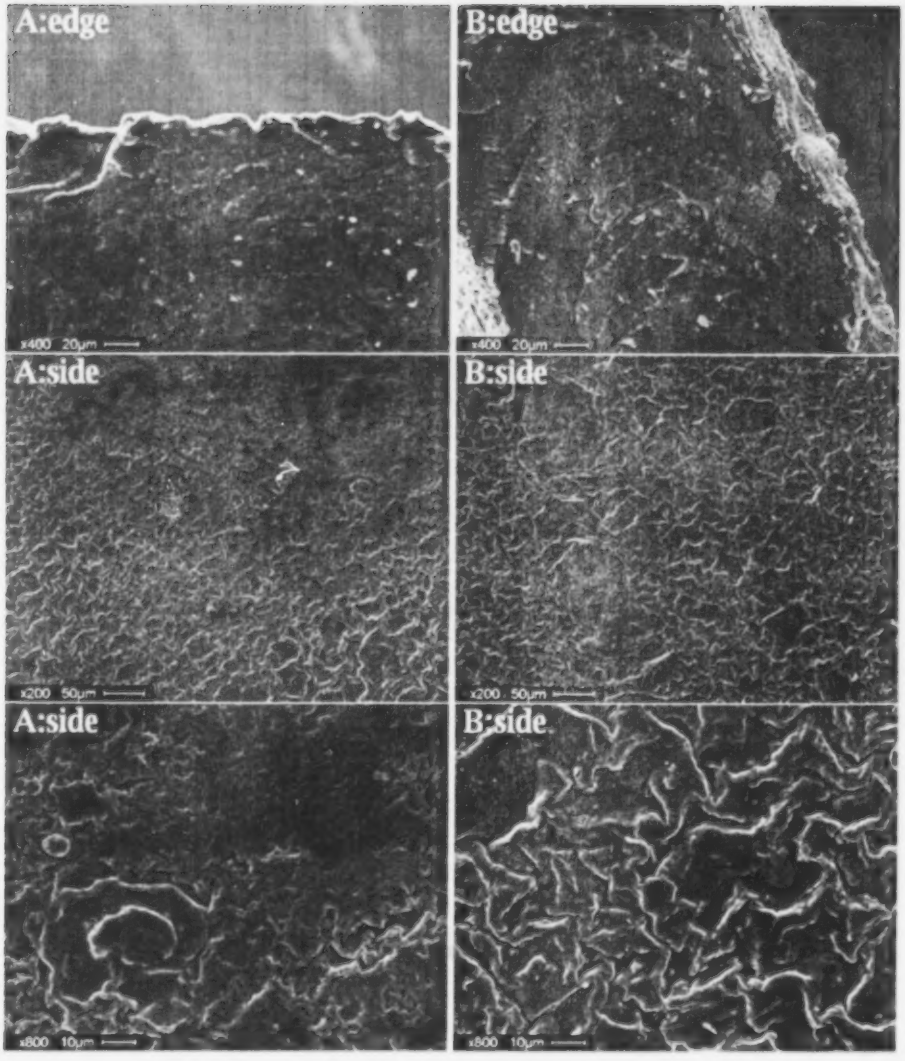

Figure 13: *SEM edge and surface view pictures of polypyrrole-latex films not coated with carbon: (a) prior to stretching, and (b) after stretching.*

value differs only slightly from the one reported in the literature, 1480 cm^{-1} [11]. The presence of polybutadiene, and polypyrrole together in the sample indicates that polymerization occurred throughout the sample, and not just on the surface of the latex. The FTIR spectra of the interpenetrating polymer network does not exhibit any characteristic vibrations indicating the presence of phosphomolybdic acid [5,8]. The characteristic peak positions associated with phosphomolybdic acid,

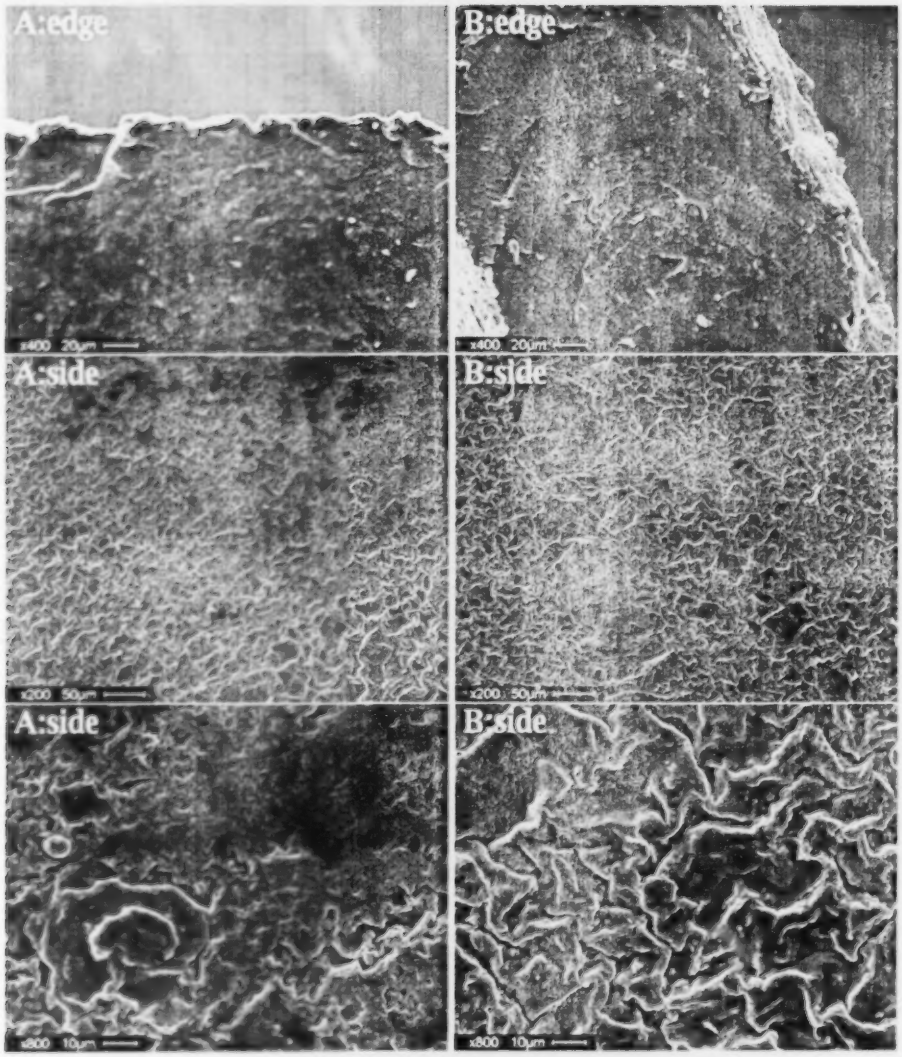

Figure 13: *SEM edge and surface view pictures of polypyrrole-latex films not coated with carbon: (a) prior to stretching, and (b) after stretching.*

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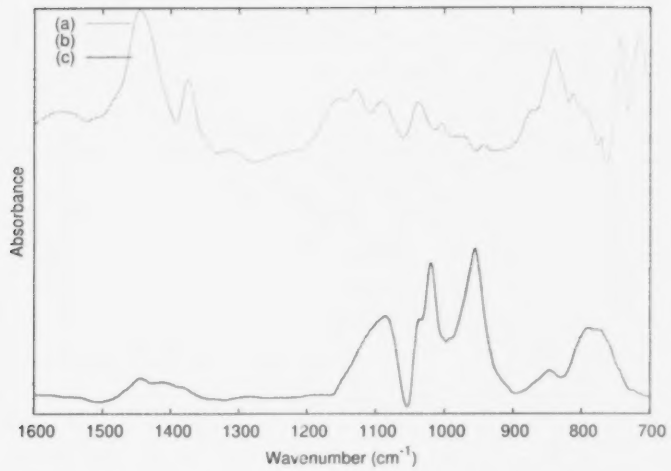

Figure 14: *FTIR spectra of (a) plain latex, (b) latex loaded with phosphomolybdic acid, (c) interpenetrating polymer network.*

if present, would include a P-O stretch at 1065 cm^{-1}, M=O terminal at 963 cm^{-1}, M–O–M corner shear at 867 cm^{-1}, and M–O–M edge shear at 784 cm^{-1} [5, 8]. This suggests that all excess phosphomolybdic acid was washed out of the latex film upon completion of the polymerization process and rinsing. These spectra support the conclusion that an interpenetrating polymer network was successfully formed throughout the polybutadiene host polymer.

4.3 Summary

FTIR spectra and SEM images demonstrate that polypyrrole has grown on the surface and within the latex matrix, thus indicating the successful formation of an interpenetrating polymer network.

The success of procedure four may be attributed to the following conditions: The latex samples were soaked in phosphomolybdic acid before being suspended in a closed system where polymerization was to occur. The loaded latex samples were not rinsed before being suspended. Furthermore, the latex loaded in phosphomolybdic acid polymerized most successfully when not being directly exposed to monomer solution. Rather, the monomer solution was allowed to volatize up to the suspended samples in a closed system. For successful networks to be formed, it is also crucial to have a substantial amount of THF present in the system. This is to keep the latex samples swelled, thus allowing polymerization throughout the sample to occur.

After stretching the latex, fractures are observed in the sample (Figure 13. While there was no mechanical failure associated with the presence of the polypyrrole, the fracturing will likely affect the conductivity of the sample.

5 Goal 3

To extend the general synthetic strategy, to a new polymer system. Specifically, we focus on polythiophene and show that spin-coated polythiophene films exhibit similar morphologies, structures, and electrochemical behaviour as the electrochemically grown polythiophene films. In addition, we focus on the role of kinetics during the chemical polymerization of thiophene, bithiophene, and terthiophene with phosphomolybdic acid in bulk solution.

5.1 Background

Polythiophene is a polymer attracting considerable attention due to its environmental stability, and relatively high electrical conductivity. It has proven to be a useful material in emerging technologies, such as the development of charge dissipation films, light-emitting diodes, and volatile organic gas sensors [12]. The advantage of chemically preparing polythiophene is that the process does not require a conducting substrate. Another successful method of preparing polythiophene films reported in the literature is by plasma polymerization. Several research groups [13] are currently working on the plasma polymerization of thiophene. While plasma polymerization produces films that are smooth and uniform, due to a higher degree of cross-linking and branching reactions, films exhibit significantly lower conductivities. In this work, chemically generated polythiophene films are produced that exhibit both good conductivities, as well as relatively smooth and homogeneous thin films.

5.2 Experimental design

5.2.1 Synthesis

The parameters necessary to reproduce the electrochemical polymerization of thiophene, bi-thiophene, and ter-thiophene were optimized, and compared with the literature data (Figure 15). The peak potentials obtained for the oxidation of thiophene and it oligomers were consistent with literature values [14]. The formal potential of phosphomolybdic acid (the oxidant used in this work) is 0.4V [15].

When preparing chemically spin coated polythiophene films, the conjugation length of the monomer was varied by using either bithiophene, or terthiophene with phos-

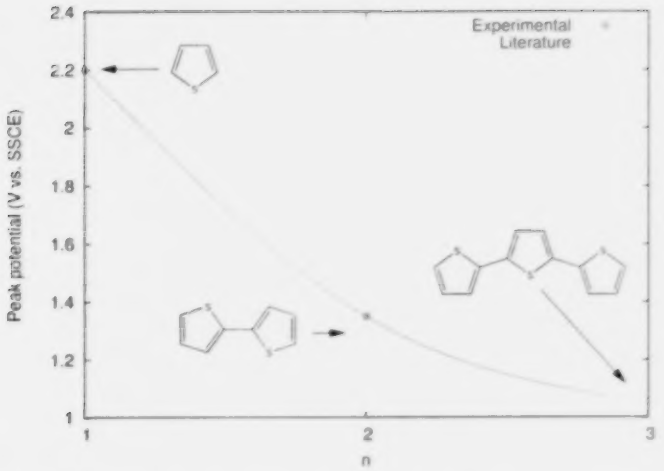

Figure 15: *Peak oxidation potential of thiophene, bithiophene, and terthiophene.*

phomolybdic acid as oxidant. Acetonitrile was the solvent used to spin-coat polythiophene. A few trials were performed with THF as the solvent; however these trials yielded non-homogeneous films with poor conductivity.

5.2.2 Method

The polymerization mixture for synthesizing spin-coated polythiophene consisted of 0.1 M of bithiophene in acetonitrile and 0.05 M of phosphomolybdic acid in acetonitrile. The chemically grown films were spin coated with the following settings: 1000 RPM with 1000 RPM/s acceleration for a duration of 10 seconds.

Upon completion of spin coating, the chemically prepared films were rinsed in acetonitrile to remove the phosphomolybdic acid, unreacted monomer, and oligomers. The films were then left to dry at room temperature. The films at this point were found to be in the reduced form, (the non-conducting state). As a result, an additional step to the spin-coating process was executed in order to chemically oxidize the films. Polythiophene films spin coated on non-conducting substrates such as glass were chemically oxidized by rinsing the films with $FeCl_3$ solution. The films were thus converted into their conducting form (oxidized state). Following oxidation, the films were once again rinsed in acetonitrile. The films were left to dry at room temperature between each rinsing procedure.

When electrochemically growing the polymer from bithiophene monomer, the potential cycling range was from 0.0 V to 1.0 V, and the film was grown in 4 segments. The scan rate was 0.1 $V\,s^{-1}$. When performing voltammetry studies on prepared

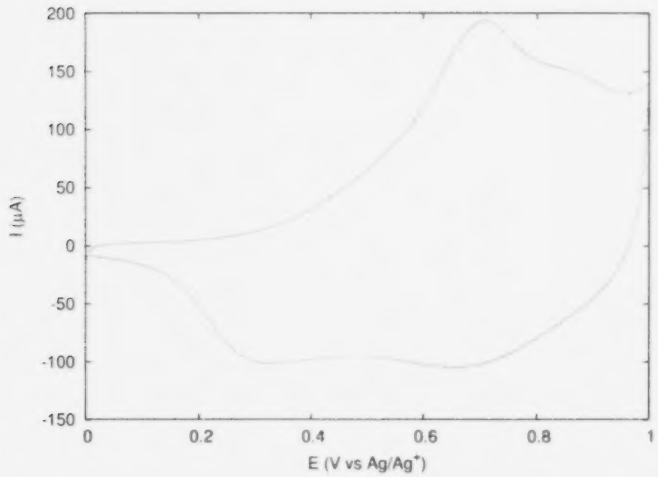

Figure 16: *Cyclic voltammogram on polythiophene grown electrochemically on ITO in 0.10 M $TBAPF_6$/acetonitrile. Scan rate = 0.05 V s^{-1}.*

films, the potential cycling range was also from 0.0 V to 1.0 V, with a scan rate of 0.05 V s^{-1}.

The kinetics of the chemical polymerization of bithiophene and terthiophene (and the attempted chemical polymerization of thiophene) with phosphomolybdic acid as oxidant were studied in bulk solution by taking UV-vis spectra of each sample mixture every 30 seconds for varying durations. Approximately 3 ml of the reaction mixture was placed in a quartz cuvette for analysis. The solvent used in the reactions shown below was acetonitrile, unless otherwise specified.

5.3 Results and Discussion

In order to verify that polythiophene was indeed produced during spin-coating, the electrochemical behavior (using ITO substrate), and FTIR spectra of the films were studied and compared to the electrochemically grown film. These studies also confirmed the absence of phosphomolybdic acid in the spin-coated film upon completion of the polymerization and rinsing process.

The cyclic voltammetry of the electrochemically (Figure 16) and chemically (Figure 17) prepared films appear similar, which suggests that the compositions of the films are indeed very similar. Both films were prepared from bithiophene monomer. Upon completion of the polymerization process, the film was rinsed in acetonitrile in an attempt to remove any unreacted oxidant and monomer. The electrochemically generated film was prepared in the absence of phosphomolybdic acid, and

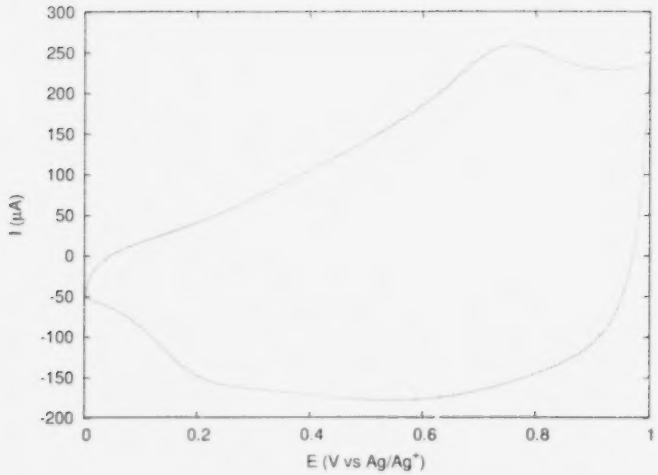

Figure 17: *Cyclic voltammogram on polythiophene spin coated on ITO in 0.10 M $TBAPF_6$/acetonitrile. Scan rate = 0.05 $V s^{-1}$.*

thus serves as a control experiment demonstrating the voltammetry of polythiophene prepared in the absence of phosphomolybdic acid. There is no redox behaviour present in the chemically grown film that would suggest the presence of phosphomolybdic acid (see Figure 17).

The FTIR absorption spectra of the chemically and electrochemically prepared films also appear very similar. Films prepared in both manners exhibit characteristic vibrations of polythiophene. The films absorb at 1500 cm^{-1}, and 825 cm^{-1}, which corresponds with literature values for the absorption of films prepared by both methods [13, 16]; the FTIR spectra demonstrates that polythiophene was indeed spin-coated onto the ITO substrate, as opposed to low mass oligomers. The peak at 825 cm^{-1} is representative of the aromatic C–H out of plane deformation. The characteristic peak positions associated with phosphomolybdic acid, (if present) would include a P–O stretch at 1065 cm^{-1}, M=O terminal at 963 cm^{-1}, M–O–M corner shear at 867 cm^{-1}, and M–O–M edge shear at 784 cm^{-1} [5,8]. The spin-coated film lacks the characteristic vibrations associated with the presence of phosphomolybdic acid.

Cyclic voltammetry and FTIR spectra studies indicate that phosphomolybdic acid is not present in the chemically spin-coated film upon completion of polymerization and the rinsing process. This is consistent with the data observed in the first section of this report.

In order to study and characterize the chemically generated polythiophene films, *in situ* spectroelectrochemistry measurements were performed. To further study the

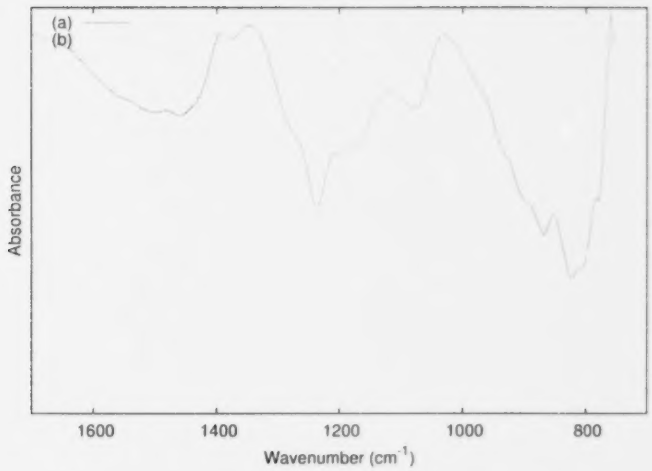

Figure 18: *FTIR spectra of polythiophene: (a) spin coated on ITO, (b) electrochemically grown on ITO.*

kinetics of chemical polymerization, the UV-vis spectra was taken of the polymerization mixtures in bulk solution.

Upon preparation of the spin coated polythiophene films chemically grown in the presence of phosphomolybdic acid (from either bithiophene or terthiophene monomer units) the films were in their reduced state, with an absorbance maximum at approximately 600 nm. To oxidize the films, they were rinsed in a 0.01 M solution of $FeCl_3$ in acetonitrile. The absorbance maximum subsequently shifted to a value of approximately 450 nm indicating that the polymer was in its oxidized, conducting state.

In Figure 19, the sequentially decreasing peak at $\approx$450 nm corresponds to oxidation of an electrochemicaly prepared polythiophene film. The same phenomenon is observed in Figure 20 for a chemically grown film, although the peak is somewhat broader and occurs at slightly longer wavelengths. This indicates that the chemically grown film is of equal or better quality than the electrochemically grown one; shorter conjugation lengths lead to this $\pi - \pi^*$ transition at shorter wavelengths.

As expected, the polymerization kinetics for the monomer, dimer and trimer are different. The polymerization of thiophene was unsuccessful using phosphomolybdic acid as oxidant. The redox potential of thiophene is too high for phosphomolybdic acid to act as an efficient oxidant. Even after a period of 12 hours, no polymer was formed in solution.

Under the conditions described above, both bithiophene and terthiophene resulted

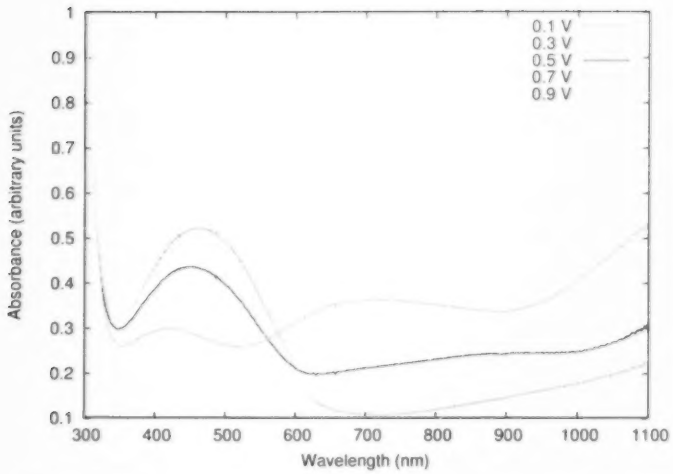

Figure 19: *In situ spectroelectrochemistry of polythiophene on ITO, grown electrochemically from bithiophene monomer. Applied potentials range from 0.1 V to 0.9 V.*

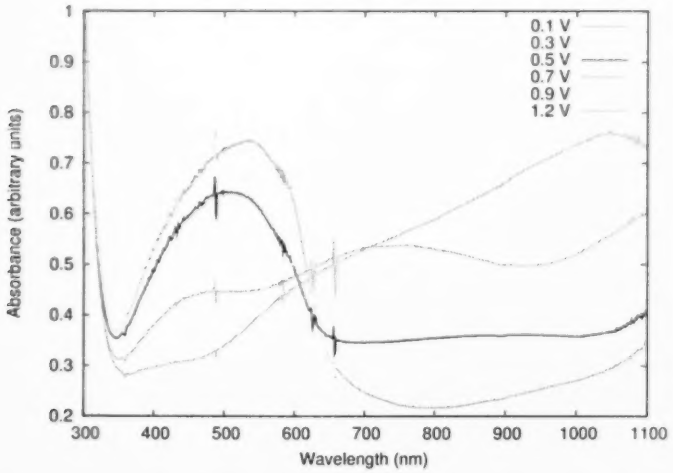

Figure 20: *In situ spectroelectrochemistry of polythiophene on ITO, grown chemically from bithiophene monomer. Applied potentials range from 0 V to 1.2 V.*

in successful polymerization of polythiophene in solution. Upon successful formation of chemically generated polythiophene, a peak at $\approx$700 nm is observed. This peak is characteristic of polythiophene in its reduced state, and as a result, the additional step of rinsing the films in a stronger oxidant, (such as $FeCl_3$) is needed. It has been reported that during the electrochemical polymerization of polythio-

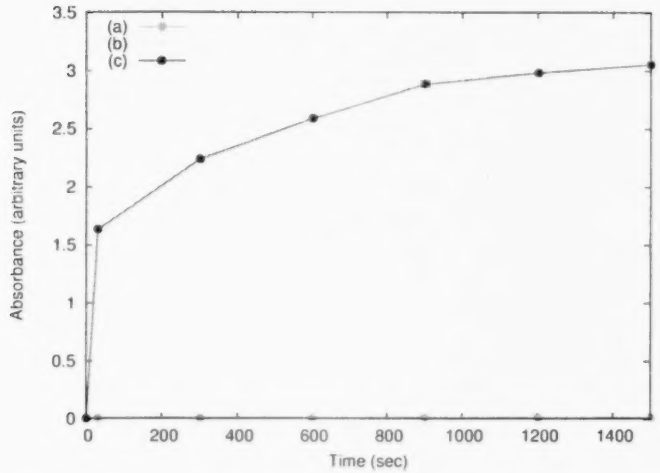

Figure 21: *Absorbance vs. time at 700 nm, indicating the formation of polythiophene in solution. Polymerization of the following monomer units (0.1 M) with phosphomolybdic acid (0.05 M): (a) thiophene, (b) bithiophene, and (c) terthiophene.*

phene from terthiophene in propylene carbonate, an absorption band is observed at ≈600 nm. This film is said to be in its neutral (non-conducting) form [17]. Based on this comparison, it is reasonable to postulate that under the conditions described above, the peak growing at ≈700 nm corresponds to the formation of polythiophene in its reduced form. With the spectrum obtained, absorbance was plotted as a function of time with the intent of investigating the kinetics of the reaction. Figure 21 shows that the rate of polymeration follows the trend in oxidation potential shown in Figure 15 where the trimer polymerizes the most rapidly.

An unsuccessful attempt at polymerization involved bithiophene using THF as solvent. THF as solvent was used in a few trials, however this solvent produced films with non-homogeneous surfaces, and low conductivities. THF is more volatile than acetonitrile, and thus perhaps it evaporates too quickly, before the polymerization reaction has adequate time to take place. However, even after allowing the reaction mixture sit in a closed system from 30 minutes up to 3 hours before spin coating, the homogeneity of the resulting films was still poor. When the UV-vis kinetics of bithiophene and phosphomolybdic acid in THF were studied, no well-defined peak occurred in the region of 700 nm or elsewhere. This indicates that polythiophene is not chemically generated in the presence of THF.

To further investigate the kinetics of the monomer (bithiophene or terthiophene) and oxidant mixture in solution, the concentration dependence of the polymerization

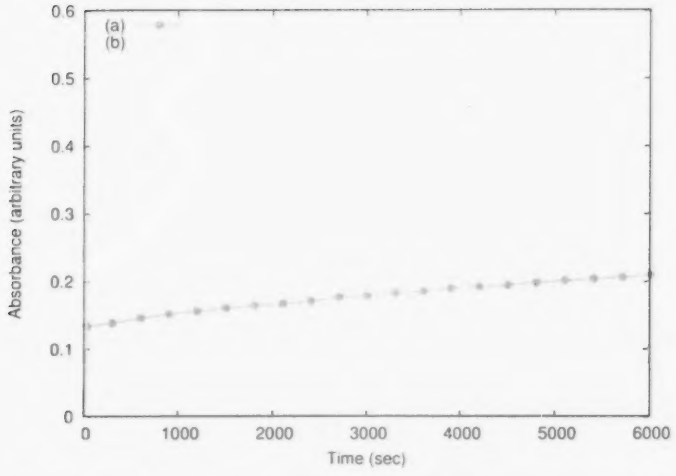

Figure 22: *Plot of absorbance vs. time for bithiophene/phosphomolybdic acid: (a) 0.1 M/0.025 M, (b) 0.1 M/0.05 M phosphomolybdic acid.*

rate was explored. Specifically, the polymerization of biothiophene was observed while keeping the monomer concentration constant and varying the concentration of phosphomolybdic acid. As seen in Figure 22, increasing the concentration of phosphomolybdic acid does in fact increase the rate of reaction.

5.4 Summary

Through the use of cyclic voltammetry and spectroelectrochemical studies, it has been demonstrated that polythiophene films can be chemically synthesized by spin coating mixtures containing bithiophene. The resulting films appear to exhibit similar morphologies, structures, and electrochemical behaviour as the electrochemically grown polythiophene films.

The preferred solvent for carrying out reactions in this experiment was acetonitrile. It appears that THF was too volatile to yield smooth and homogeneous polythiophene films. UV-vis kinetics studies fail to demonstrate that the polymer is even growing in THF solution, (based on lack of the characteristic peak at 700 nm, indicating the formation of polythiophene for the identical reaction carried out in acetonitrile.)

The kinetics for the reaction of bithiophene with phosphomolybdic acid in acetonitrile, indicate that increasing the concentration of phosphomolybdic acid in the polymerization mixture does in fact increase the rate of reaction, (as is true for the polypyrrole system). This may be another parameter which can be varied to

manipulate the polymerization reaction and in turn the properties of the films.

While the amount of phosphomolybdic acid present in the reaction mixture affects the rate of reaction, when spin-coating polythiophene films, cyclic voltammetry and FTIR spectral studies indicate that phosphomolybdic acid is absent from the chemically spin coated film after rinsing.

6 Conclusions

The present work demonstrates that the general synthetic strategy used to coat insulating materials with a conducting polymer has been successfully extended to a new system. Chemically synthesized, spin-coated polythiophene films exhibit morphologies, structures, and electrochemical behaviour similar to the electrochemically grown films. Polythiophene has been successfully spin-coated onto a non-conducting substrate, producing films that exhibit some conductivity, as well as relatively smooth and homogeneous surface features. In the case of bithiophene, terthiophene and pyrrole, phosphomolybdic acid has a substantial redox potential to initiate chemical polymerization. Moreover, upon completion of the polymerization process, excess phosphomolybdic acid is readily rinsed away.

Similarly, phosphomolybdic acid is readily rinsed away in the polypyrrole system. In this system, x-ray diffraction patterns demonstrate that the polymer adopts the morphology of the polyoxometalate cluster, and maintains this morphology after the phosphomolybdic acid has been rinsed away.

7 Future work

Based on the results of this report, several major strategies should be pursued. Phosphomolybdic acid as an oxidant does not have a redox potential sufficiently positive to generate polythiophene from thiophene monomer. One could tune the redox potential of the polyoxometalate in solution. This may be achieved by replacing the molybdenum metal cluster of the polyoxometalate with, for example, vanadium. This will then impact the initial concentrations of the radical cations in solution, and in turn the initial rate of polymerization.

It would be desirable to produce polythiophene films in their oxidized form, while spin coating the reaction mixture onto non-conducting substrates. The need to chemically oxidize the made polythiophene films in an additional step upon completion of polymerization is not ideal. Furthermore, it would be interesting to determine the morphology of the polymer once the phosphomolybdic acid is rinsed away. It is hypothesized that the polythiophene film adopts the morphology of the

polyoxometales clusters, and maintains this morphology after the phosphomolybdic acid is rinsed away. (This was demonstrated to be the case with the polypyrrole system).

It would be desirable to prepare interpenetrating polymer networks with higher conductivity values. At the present time, it appears that polymerization on the surface of the latex is relatively fast, resulting in only a small amount of monomer diffusing inside the latex. Several experiments should be performed in order to increase the amount of phosphomolybdic acid that is loaded into the latex. Increased loading of phosphomolybdic acid may allow for more monomer to diffuse inside the latex, resulting in more polymer forming throughout the structure, and thus higher conductivity values may be achieved. It would also be interesting to pursue thermal studies, as well as some mechanical properties of the resulting interpenetrating polymer networks.

8 Experimental Details

8.1 Chemicals and Materials

The Phosphomolybdic acid hydrate ($H_3PMo_{12}O_{40}{\cdot}xH2O$, FW: 1825.24), Pyrrole (C_4H_5N, FW: 67.09), Thiophene (C_4H_4S, FW: 84.14), 2,2′-bithiophene ($C_8H_6S_2$, FW: 166.26), 2,2′ :5′,2″-terthiophene ($C_{12}H_8S_3$, FW: 248.39), Tetrahydrofuran (THF, HPLC grade), Acetonitrile (CH_3CN, HPLC grade), and Tetrabutylammonium hexafluorophosphate ($TBAPF_6$, $[C(CH_3)_3]_4NPF_6$, FW: 387.44) were purchased from Aldrich and used without any further purification. Lithium perchlorate ($LiClO_4$, FW: 106.4) was obtained from BDH and used without any further purification. The latex films, obtained from Ansell, were cut in a circular shape with a diameter of 1-1/4 inch. In order to remove starch and any other impurities on the surface, the films were sonicated twice, first in deionised water for 20 min (every 5 min the deionised water was replaced) and then in methanol for another 20 min. These starch-free films were first dried in air under ambient conditions and then under vacuum overnight and weighed.

8.2 Instruments

8.2.1 Electrochemical apparatus

All Cyclic voltammetric measurements were performed using a CH Instrument, CHI-660 workstation. A three-electrode set up using a platinum coil auxiliary electrode, a Pt working electrode, and an $Ag/AgNO_3^-$ reference electrode. All measurements were performed using either $LiClO_4$ or $TBAPF_6$ (0.1 M) in acetonitrile as electrolyte.

8.2.2 X-Ray Diffraction

Step Scan X-ray Diffraction data were collected at room temperature with a Philips automated diffractometer system PW1710. The PW1710 uses a PW1050 Bragg-Brentano goniometer equipped with incident- and diffracted-beam Soller slits, 1.0° divergence and anti-scatter slits, a 0.2 mm receiving slit and a curved graphite diffracted-beam monochromator with a Cu Kα radiation. The step-scan data were collected using MDI DataScan software and read directly into MDI's Jade+ v.6.5 XRD software for data processing. Polypyrrole films were prepared by spin coating solutions containing pyrrole and phosphomolybdic acid onto zero background quartz slides. All slides were rinsed with THF in order to remove any trace of reduced Phosphomolybdic acid and analyzed immediately. The patterns obtained were compared against pure phosphomolybdic acid in its oxidized and reduced form.

8.2.3 Scanning Electron Microscopy

Scanning Electron Microscopy data was collected using a SEM fitted with a Kevex 7000 EDS spectrometer that provides '3-D' images at high magnifications, BSE and secondary-electron images. It has a 4-quadrant semiconductor BSE detector.

8.2.4 FTIR measurements

FTIR measurements were recorded using a Thermo Nicolet Magna IR spectrometer at room temperature. Infrared spectra of samples ground in KBr pellets (FTIR grade, Aldrich) obtained from an accumulation of 100 interferograms at a resolution of 4 cm^{-1}. PM-IRRAS spectra were collected from an accumulation of 300 interferograms at a resolution of 8 cm^{-1}. ITO was positioned at 63° with respect to the detector. Thunderdome spectra were collected from an accumulation of 100 interferograms at a resolution of 4 cm^{-1}. The FTIR data were then analyzed with Omnic v6.2 (Thermo Electron Corporation).

8.2.5 UV-VIS measurements

UV-VIS measurements were collected at room temperature using a UV-VIS Chem Station Rev. A.09.01[76] from Agilent Technologies. The UV-VIS data were then transformed into ASCII format and subsequently analyzed with Excel.

9 Symbols and Abbreviations

BES Back electron scattering

EDS Energy dispersion (x-ray) spectroscopy

FTIR Fourier transform infrared

FW Formula weight

ITO Indium tin oxide; a glass slide coated with ITO

PM-IRRAS Polarization modulated-infrared reflectance absorbance spectroscopy

SEM Scanning electron microscopy

$TBAPF_6$ Tetrabutylammonium hexafluorophosphate

THF Tetrahydrofuran

UV-vis Ultraviolet-visible spectroscopy

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It has been over twenty-five years since Heeger, MacDiarmid and Shirakawa found that polyacetylene could be endowed with near-metallic electrical conductivity following oxidation (or *doping*) with iodine. Since then, there has been a surge in investigation of conducting polymers, most commonly polythiophene, polypyrrole, polyaniline, or their derivatives. Numerous conducting polymer applications have been proposed, ranging from molecular electronics to anti-corrosive agents. The importance and potential impact of the discovery of conducting polymers resulted in Heeger, MacDiarmid and Shirakawa receiving the Nobel Prize in Chemistry (2000). Despite the promise of these new materials, very few viable technologies have emerged from the laboratory proof-of-concept level. It is widely known that one of the most important causes of this failure is the lack of processability of conducting polymers. Bulk polymer can be synthesized in solution by oxidation of the monomer resulting in radical coupling, with the desired product precipitating rapidly as an amorphous powder. Precipitation is driven by π-stacking and Coulombic effects leading to very strong interchain interactions. This in turn precludes conventional thermoplastic or solution processing methods. Several elegant approaches have been developed over the years to reduce π–π interactions in order to generate soluble conducting polymers, however these approaches invariably lead to lower conductivities (due to decreased p-orbital overlap along the backbone) and increased costs. This document describes an alternate, general-purpose route to preparing conducting polymers under processible conditions.

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